Traditional and emerging perfluoroalkyl substances in the Cape Fear River Watershed, North Carolina: Occurrence and fate during conventional and advanced water treatment processes

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Abstract

Because of their persistence, bioaccumulation potential, and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid and perfluorooctane sulfonate are being replaced with short-chain PFASs and fluorinated alternatives. Limited information is available on the occurrence and behavior of these replacement chemicals. This study investigated traditional and emerging PFASs in terms of their (1) occurrence in the Cape Fear River watershed of North Carolina, USA, (2) fate through a full-scale water treatment plant, and (3) removal by powdered activated carbon (PAC) adsorption. Seven perfluorocarboxylic acids (PFCAs), three perfluorosulfonic acids (PFSAs), and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs) were studied. Concentrations of perfluorohexanoic acid, perfluoroheptanoic acid and perfluorooctane sulfonic acid reached >200 ng/L (maximum 346 ng/L) in surface water. Downstream of a PFAS manufacturing site, seven PFECAs were detected. The only PFECA for which an authentic standard was available, perfluoro-2-propoxypropanoic acid (trade name "GenX"), was detected at an average concentration of 631 ng/L, approximately five times that of the average summed PFCA and PFSA concentrations (129 ng/L) at that location. Among the PFECAs without available authentic standards, three exhibited large chromatographic peak areas (up to 15 times the GenX peak area), suggesting these emerging PFASs are present at possibly ~~high~~ higher concentrations. Samples collected in a drinking water treatment plant illustrated that neither traditional nor emerging PFASs were removed by coagulation/flocculation/sedimentation, raw and settled water ozonation, biological activated carbon filtration, or disinfection by medium pressure ultraviolet lamps and free chlorine. PAC adsorption data illustrated the adsorbability of PFASs increased with increasing chain length. PFSAs exhibited a higher affinity for PAC than PFCAs with the same chain length. Replacing one CF_2 group with an ether oxygen atom decreased the affinity of PFASs for PAC, such that a mono-ether of a given chain length had a lower affinity than the corresponding PFCA. The replacement of additional CF_2 groups with ether oxygen groups did not result in additional affinity changes among the studied PFECAs.

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Introduction

Perfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water and stain repellents, firefighting foams, and food-contact paper coatings. Until 2000, use of PFASs was dominated by long-chain PFASs, such as perfluorocarboxylic acids (PFCAs) with 7 or more carbon atoms and perfluorosulfonic acids (PFSAs) with 6 or more carbon atoms.[1] Increasing evidence about ecotoxicological and human health effects associated with exposure to long-chain PFASs has led to increased regulatory attention. For example, recently the U.S. Environmental Protection Agency (USEPA) established a lifetime health advisory level of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) concentrations in drinking water.[2,3] Over the last decade, production of long-chain PFASs has been on the decline, and manufactures are moving towards short-chain PFAS and fluorinated alternatives.[4-6] However, little information is available about properties and biological effects of these substitutes.[4] Some fluorinated alternatives have been identified recently,[5] but most remain unknown. It has been reported that the majority of the organofluorine mass loading to the aquatic environment remains unidentified, suggesting the extensive existence of unknown fluorinated organic compounds in the environment.[7-9]

One class of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), ~~are~~ have been recently identified, including perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)).[10] The ammonium salt of PFPrOPrA is a known PFOA alternative that has been produced since 2010, with the trade name of "GenX".[11] These compounds were detected in the Cape Fear River (CFR, North Carolina, USA) and in finished drinking water derived from the CFR water downstream of a PFAS manufacturing facility. CFR watershed is the largest watershed in NC (23,700 km^2), providing drinking water source for more than 120 public water systems serving almost 1.5 million North Carolinians.[12] To the knowledge of the authors, the only other available PFECA occurrence data are for PFPrOPrA in Europe and China.[13]

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The strong C-F bond makes PFCAs and PFSAs refractory to abiotic and biotic degradation.[14] Reports show that PFASs are not removed by most water treatment processes.[15-19] Furthermore, if PFAS precursors (e.g., fluorotelomers) are present, they can be transformed into PFCAs and PFSAs in some oxidative treatment processes such that PFCA and PFSA concentrations in finished drinking water can be higher than in the source water.[18] Methods capable of removing PFCAs and PFSAs include nanofiltration,[20] reverse osmosis[18], ion exchange and activated

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carbon.[20,21] The addition of oxygens to the carbon chain in PFECAs was designed to enable "very rapid bioelimination".[11] However, ~~no~~ little information is available on the pharmacokinetic behavior or the fate and transport of PFECAs in the environment or engineered systems.

The objectives of this research were to identify and quantify the presence of traditional and emerging PFASs in a drinking water source, assess their removal in an advanced drinking water treatment plant, and evaluate PFAS adsorbability by powdered activated carbon (PAC).

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Rae et al., 2015 Evaluation of chronic toxicity and carcinogenicity of ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate in Sprague-Dawley rats. Toxicology Reports pp 939-949

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Materials and Methods

Analytical standards. PFASs studied in this research are listed in Table S1 in SI. Native and isotopically labeled PFAS standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA).

Water samples: Water samples were collected in the CFR watershed (Figure S2 in SI) from June to November 2013. Surface water samples (238 in total) were collected at the intakes of drinking water treatment plants (DWTPs) of three communities in the watershed. In August 2014, grab samples along the treatment train of the DWTP in community C were collected. On the same day, surface water downstream of a PFAS manufacture site was collected for adsorption experiments described below. Field sampling quality assurance was performed as described in previous studies.[10,22]

Adsorption experiments: Batch kinetic tests were conducted to evaluate PFAS adsorption by PAC. Tests were conducted in amber glass bottles containing 0.45 L of filtered surface water collected downstream of a PFAS manufacture site (Figure S2 in SI). A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus OH, mean diameter: 12 μm, BET surface area: 1460 m^2/g) was used at doses of 30, 60 and 100 mg/L.

PFAS quantification: PFAS concentrations in surface water samples and from the adsorption tests were measured using liquid chromatography tandem mass spectrometry (LC-MS/MS) by large volume (0.9 mL) direct injection. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC/MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5μm 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient was shown in Table S2 in SI. MS transitions for PFAS analytes and internal standards (mass-labeled PFASs) are shown in Table S3 in SI. The quantification limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid (PFDA), and 10 ng/L for other traditional PFASs and PFPrOPrA. PFECAs without analytical standards were not quantified, but their chromatographic peak areas are reported instead.

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PFAS concentrations along the DWTP treatment train were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Details of the methods is described elsewhere.[22] Method QL is 0.2 ng/L for all PFASs with analytical standards, and peak areas were recorded for PFECAs without standards.

Results and Discussion

PFAS occurrence in drinking water sources: PFAS concentrations in surface water intakes of three public water systems in the CFR watershed are shown in Figure 1. In communities A and B, only traditional PFASs were detected (average ∑ PFASs at 389 ng/L in community A, 117 ng/L at community B). Detailed concentration data are shown in Table S4 in SI. In community A, PFCAs with 4-8 carbons, as well as PFOS and perfluorohexane sulfonic acid (PFHxS) were all detected with median concentrations above the QLs. Mean and median concentrations were 49 and 29 ng/L, respectively, for PFOS, and 46 and 34 ng/L, respectively, for PFOA. During the 127-day sampling campaign, there were 57 days when the sum concentration of PFOS and PFOS was above the USEPA drinking water lifetime health advisory level (70 ng/L). Results in community A indicate one or more important PFAS sources ~~were~~ are located upstream. The PFAS concentrations in community B were lower than in community A, with median concentrations < QLs for most of the PFASs. The lower PFAS concentrations in community B is principally a result of dilution by tributaries.

In community C (downstream of a PFAS manufacturing site), traditional PFAS concentrations were low, and only median perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) concentrations were >QLs. However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). In six samples with PFPrOPrA concentrations beyond the upper limit of the calibration curve (750 ng/L), concentrations were estimated through extrapolation. The average PFPrOPrA concentration (631 ng/L) is approximately five times of the average summed PFCA and PFSA concentrations (129 ng/L). The structures of other PFECAs had not been identified at the time samples were collected and analyzed in 2013 so no data ~~of~~ for them are available.

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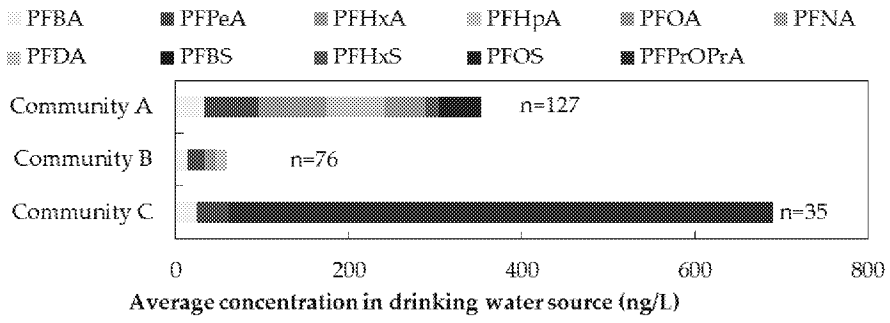

Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and November 2013. Individual samples with concentrations < QLs were considered as 0 when calculating averages. Average concentrations < QLs were not plotted.

PFAS fate in an advanced DWTP: To investigate whether PFASs can be removed from the impacted source water, samples from the DWTP of community C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and several advanced drinking water treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, biological activated carbon (BAC) filtration) removed neither traditional PFASs nor fluorinated alternatives. Results for traditional PFASs agree with previous reports.[15-19] Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA, PFMOAA may have increased after ozonation, possibly due to the oxidation of precursor compounds,[18] and disinfection with medium pressure UV lamps (located the between BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but the extent of removal was limited.

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Results in Figure 2 also confirm that PFPrOPrA was present in both raw and finished water at concentrations (400-500 μg/L) much higher than traditional PFASs. Moreover, three other PFECAs (PFMOAA, PFO2HxA and PFO3OA) had peak areas 2-113 timer great than that of PFPrOPrA, suggesting these PFECAs may be present at concentrations orders of magnitudes higher. The possible existence of high levels of emerging PFASs suggests the necessity of incorporating them into routine monitoring.

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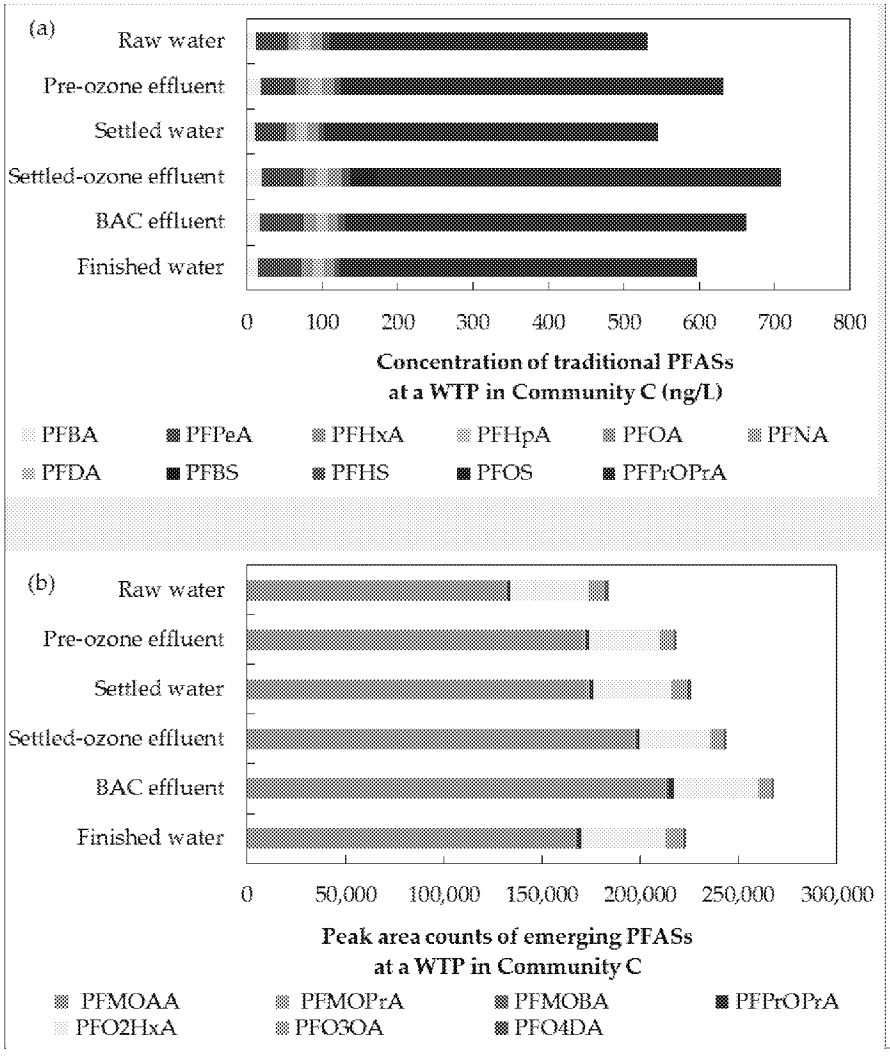

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Figure 2. Fate of (a) traditional PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Due to the lack of authentic standards, the emerging PFASs are shown as chromatographic peak area counts from LC-MS/MS analyses. PFPrOPrA data are shown in both figures for reference. Compounds with concentrations <QLs were not plotted.

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PFAS removal by PAC adsorption: It has been shown that PAC is effective for removing long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length. [17, 18, 21] To date, it is unclear, however, how the existence of one or more ether groups in PFECAs impacts adsorbability. Batch adsorption tests were conducted using surface water containing ~1000 ng/L PFPrOPrA, and other PFECAs were detected at levels from 10% to 800% of PFPrOPrA, based on peak area. PFMOAA was detected with high peak areas using solid phase extraction method in the water sample; however, to process the large number of samples in the adsorption experiments, a more rapid direct injection method was used for the ~~LC/MS/MS~~LC-MS/MS analysis. The latter did not produce a clearly identifiable peak for PFMOAA, thus the adsorbability of PFMOAA was not evaluated in this study. However, based on the observation that shorter chain compounds were less effectively removed (Figure 3(b)), and that the PFECA with one or two more atoms than PFMOAA in the chain (i.e., PFMOPrA and PFMOBA) were poorly adsorbed to PAC, it is expected that PFMOAA removal is negligible at the tested conditions. Traditional PFAS concentrations in the surface water sample were low (from <QL to 39 ng/L) and were therefore spiked into the samples at ~1000 ng/L each to compare their adsorbability to that of PFECAs.

Adsorption test results are shown in Figure 3(a). More than 80% removal was achieved after 1 hour with a PAC dose of 100 mg/L for traditional PFCAs with carbon chain length ≥7, or with a PAC dose of 60 mg/L for traditional PFCAs with carbon chain length ≥8. PFSAs were better removed than PFCAs with the same chain length at the test conditions. At a dose of 100 mg/L, PAC removed 95% of PFO4DA, 54% of PFO3OA, but less than 40% of other PFECAs. Detailed removal percentage data at different time point are shown in Figure S3 in SI.

There are two ways to compare the affinity for PAC between different types of PFASs. Figure 3(b) shows the relationship between removal percentage and PFAS chain length (counted as the sum of carbon (including branched), ether oxygen, and sulfur atoms). The adsorbability of both traditional and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, which agrees with previous studies. PFECAs exhibited lower adsorbabilities than PFCAs of the same chain length (e.g. PFHxA vs. PFMOBA), suggesting that the replacement of one CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether oxygen groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA vs. PFO2HxA). If only the number of perfluorinated carbons is considered but not the ether oxygens, the interpretation would be different. In that case PFCAs have a higher affinity for PAC than mono-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFMOBA), but a lower affinity than multi-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFO3OA). In either

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framework, it is clear that the presence of ether groups in PFECAs changes the physiochemical properties, such as hydrophobicity of the compounds compared to the PFCAs. Consequently, it is reasonable to expect that PFECA fate and transport in natural environment or engineered systems will differ from that of traditional PFCAs, such as their sorption to soil, sediment and biota, and their removal in water or wastewater treatment processes. For example, while PFPrOPrA ("GenX") is produced as a replacement of PFOA, the adsorption data here suggested PFPrOPrA has a lower hydrophobicity than PFOA. Thus, when released to the environment, PFPrOPrA has a higher chance to remain in the aqueous phase and a bigger difficulty for removal in drinking water treatment processes.

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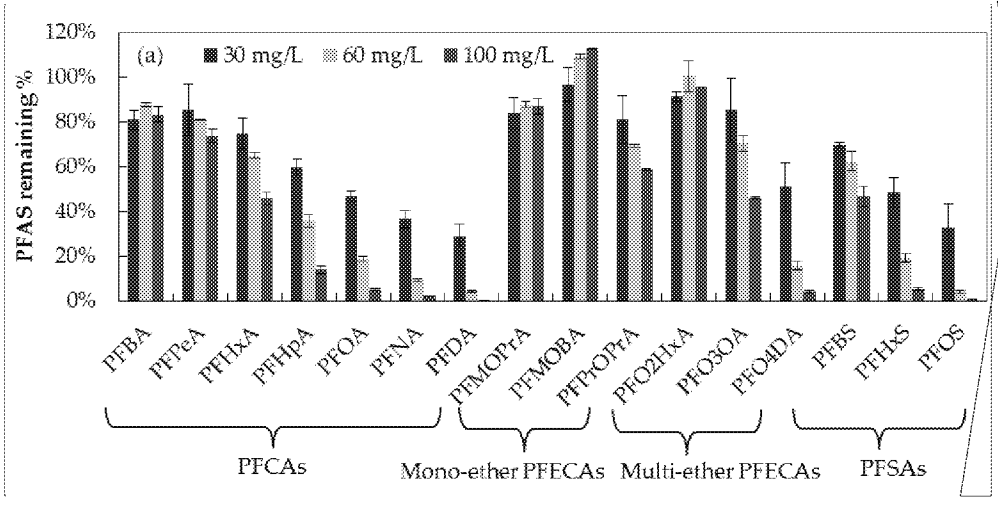

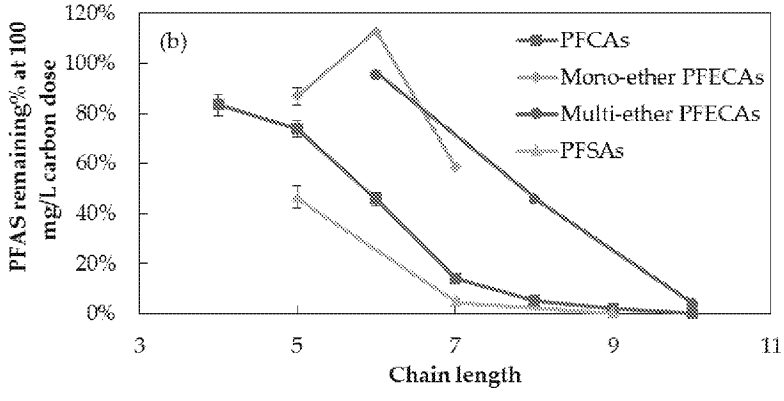

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Figure 3. PFAS adsorption to PAC from CFR water after a PAC contact time of 1 hour: fraction remaining (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. Traditional PFASs were spiked at ~1000 ng/L and the emerging PFASs were at their native concentrations. The chart shows the average of remaining PFAS percentage and the error bars show one standard deviation of replicate tests.

To the knowledge of the authors, this is the first paper reporting the behaviors of emerging PFECAs in physicochemical water treatment processes. This work documents the presence of traditional PFASs for the entire length of the CFR, the emergence of PFECAs as replacements. The relatively low concentrations of traditional PFASs in the finished drinking water in community C are consistent with data from the third unregulated contaminant monitoring rule (UCMR3) conducted by USEPA[23]. However, the detection of potentially high levels of emerging PFSAs, and the relative difficulty for water treatment processes to effectively remove not only traditional PFASs but also PFECAs, suggest the importance of a broader discharge control and contaminant monitoring. For better protection of drinking water source, additional research is needed to answer questions such as what other new PFASs might be present, what treatment processes are effective, and what risks to aquatic and human health are associated with the presence of emerging PFASs.

Acknowledgement

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